## Carbon Nanotubes: Theoretical Investigations of Growth and Mechanical Properties

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Carbon nanotubes are perhaps one of the most exciting materials to emerge from recent scientific research. This interest and excitement derives largely from their unusual structural and electronic properties, which should allow for unique applications of interest to NASA. For example, nanotube fibers have been predicted to have truly extraordinary properties, including superstrengths at one-sixth the weight of steel, extreme flexibility and resilience to strain, and very high capillary forces. Perhaps one of the more novel applications of carbon nanotubes proposed involves their use as Micro-Electrical-Mechanical Structures (MEMS): because of their extreme flexibility and regular structure, carbon nanotubes open up the exciting possibility of fabricating devices approximately 1,000 times smaller than current MEMS, again allowing for unique space-oriented applications. In our presentation, we will give a brief description of our theoretical investigations of carbon nanotubes, with a focus on aspects of their growth and their mechanical properties. The studies were a carried out with a series of complementary numerical methods covering different length and time scales, including *ab initio* and classical molecular dynamics simulations and kinetic Monte Carlo methods.

The problem of nanotube growth remains an important issue that needs to be understood if nanotubes are ever to reach their full potential as a technological material. Because carbon nanotubes form under highly nonequilibrium conditions, the kinetics of their growth represents a problem of considerable complexity. While nanotubes were first produced in carbon arcs, they have since been synthesized through laser vaporization, catalytic combustion, chemical vapor deposition and ion bombardment. Given these different methods of nanotube synthesis, it is likely that a variety of mechanisms are operating in the formation of nanotubes, and their assembly as nanoropes. However, two common features have emerged:

- 1) The type of nanotube that is produced depends on the presence/absence of catalysts: multiwalled nanotubes are the dominant product formed in the absence of metal catalysts, while single-wall nanotubes are the primary product in their presence.
- 2) Experiments have shown that during noncatalytic growth, the nanotubes actually remain open. This is surprising, because the large number of dangling bonds present at open tips definitely favor a closed-tube geometry.

A number of reasons have been given to explain the open-tube growth of carbon nanotubes. Initially, it was believed that it is the high electric fields present at the nanotube tips that keep them open during growth. However, our detailed *ab initio* simulation studies of this effect, and the subsequent development of other methods of nanotube synthesis showed that the electric field cannot be responsible for keeping the tubes open. Similarly, other reasons such as the temporary saturation of the dangling bonds with hydrogen, or thermal gradient effects may similarly be eliminated. However, there are strong indications from theory that tube closure is associated with the formation of curvature-inducing defects such as adjacent pentagon pair, and other related structures. This suggests that nanotube growth may indeed proceed in an open-ended fashion, provided that the formation of such defects is somehow suppressed. Energetically, the formation of such defects is favored only for narrow nanotubes, so that tubes with diameters greater than about 3 nm should remain open. Under conditions of catalytic growth, it is believed that the

presence of small metal particles, a root growth mechanism, or the catalytic action of Co or Ni atoms on the tips of nanotubes (the "scooter" mechanism) prevents the nucleation of such defects and leads to the formation of single-wall nanotubes with narrow diameters.

Multiwalled carbon nanotubes, however, have another important kinetic alternative open to them in the form of the so-called "lip-lip" interaction. Such an interaction arises when atoms or small clusters deposit themselves at the tips of nanotubes. These then form bridges or "spot-welds" between adjacent tube tips, which are thereby kept open for continued growth. However, a detailed set of annealing studies show that while the lip-lip interactions do indeed form, they actually aid and promote the closing of the nanotubes, rather then keep the tips open. The lip-lip interaction thereby actually forms a natural mechanism for the closing of nanotubes. We have estimated the upper bound lengths of nanotubes that can be formed in absence of catalysts as a function of tube diameter and temperature. The estimates are in good agreement with published experimental values.

Many of the possible, unique applications of carbon nanotubes are intimately related to their mechanical properties. However, while the excellent resistance of carbon nanotubes to bending and other deformations has already been observed experimentally, there has been, until recently, very little understanding of the microscopic origins of the mechanical properties of the nanotubes. Our studies show that it is the remarkable flexibility of the hexagonal network that allows the system to sustain very large bending angles, kinks, and highly strained regions. In addition, nanotubes are observed to be extremely resilient, so that large distortions via axial compression and twistings are largely due to elastic deformations with no atomic defects involved.

Of particular interest is a detailed investigations of the strain release mechanisms in armchair nanotubes under uniaxial tension. Using dynamical first-principles and classical molecular dynamics simulations, we have been able to identify the initial stages of mechanical yield in the tubes. Beyond a critical value of the tension, the system releases its excess strain via the spontaneous formation of topological defects. The first defect to form corresponds to a 90 degree rotation of the carbon-carbon bond about its center, the so-called Stone-Wales transformation, which produces a pair of coupled pentagons and heptagons (a 5-7-7-5). For example, in a (5,5) tube, the formation of such a defect costs about 2.34 eV in the absence of strain. Under a 10% strain, such a defect costs -1.77 eV, showing that this defect is effective in releasing the excess strain energy in a nanotube under tensile strain. We have further shown that these defects act as nucleation centers for the formation of dislocations in the originally ideal graphite network, and mark the onset of possible further transformations. Depending upon external conditions, both brittle (crack extension) or plastic (separation of dislocation cores and glides in opposite directions) deformation routes are possible, depending on the temperature and rate of strain. Given the energetics of the atomic transformations involved, the former can be observed under low temperature, high strain conditions, while the latter is dominant at high temperatures and low strains. We have observed each of these different behaviors in long simulations of the (10,10) tubes, thereby illustrating the different mechanical response of the system under different external conditions and providing a clear link between the atomistic models and the mesoscopic phenomena such as plasticity and fracture in the nanotube systems.